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DISSOCIATION OF POLYNITROMETHYL-
CARBINOLS. III. RATES OF EQUILIBRA-
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WATER

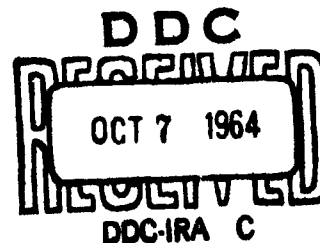
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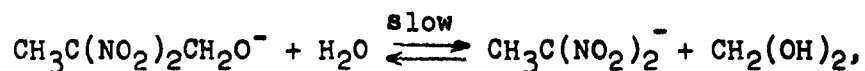
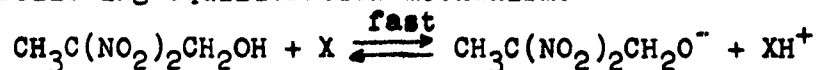


DISSOCIATION OF POLYNITROMETHYLCARBINOLS. III.
RATES OF EQUILIBRATION OF 2,2-DINITROPROPANOL
IN WATER.

by

Thomas N. Hall

ABSTRACT: The rates of equilibration of 2,2-dinitropropanol in aqueous HPO_4^{2-} - H_2PO_4^- buffers have been measured at 25.13 and 9.64°. These have been shown to be consistent with the following equilibration mechanism:



where X is a general base.

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The rates of equilibration of 2,2-dinitropropanol in water are reported and interpreted in this report as a part of a continuing study on the effect of structure on the reactivity of polynitromethylcarbinols. The work was done under Task FR-44.

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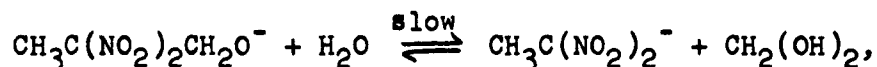
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DISSOCIATION OF POLYNITROMETHYLCARBINOLS. III.
RATES OF EQUILIBRATION OF 2,2-DINITROPROPANOL
IN WATER.

SUMMARY

The equilibration rates of 2,2-dinitropropanol have been measured in aqueous HPO_4^{2-} - HPO_4^- buffers at 25.13 and 9.64°. These rates were shown to be consistent with the following equilibration mechanism:

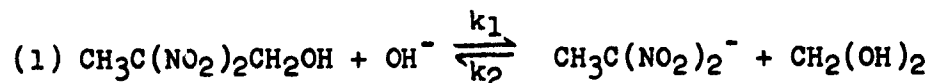


where X is a general base such as OH^- , HPO_4^{2-} , or H_2PO_4^- .

For the reaction of $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ and $\text{CH}_2(\text{OH})_2$, the bimolecular rate constant was calculated from the observed rate data to be 31.91 at 25.13° and 8.48 at 9.64°, in units of liter-mol⁻¹-min.⁻¹, and ΔH^\ddagger and ΔS^\ddagger calculated from these rate constants to 14.3 kcal-mol⁻¹, 13.7 kcal-mol⁻¹, and -13.7 e.u., respectively. The bimolecular rate constant for the reaction of $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}^-$ and H_2O could not be evaluated because the equilibrium constant for the reaction $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}^-$ is unknown. However, the product of these two constants was calculated from the observed rate data to be 1.184×10^6 at 25.13° and 3.307×10^5 at 9.64°, in liter-mol⁻¹-min.⁻¹.

INTRODUCTION

Report II of this series¹ gives evidence that, in water, the dissociation of 2,2-dinitropropanol, and of five other polynitromethylcarbinols, is an equilibrium of the form represented by equation (1)². The equilibrium constant for (1), K, was



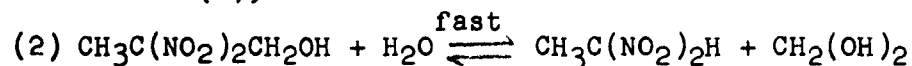
determined by measuring the amount of the carbanion $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ produced by the dissociation of a known amount of 2,2-dinitropropanol in the appropriate aqueous buffer. It was observed that the carbanion concentration increased with time, requiring as long as three hours to reach the steady state. The purpose of this study is to measure and interpret the rates of equilibration of 2,2-dinitropropanol.

EXPERIMENTAL APPROACH

An aqueous stock solution of 2,2-dinitropropanol and the appropriate buffer components were quantitatively diluted with water. The optical density, b , of this solution at λ_{max} for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ was measured versus time at constant temperature. One buffer concentration was used for each pH. The value of b is a direct measure of $[\text{CH}_3\text{C}(\text{NO}_2)_2^-]$ because the other species involved in the dissociation reaction are essentially transparent at λ_{max} for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ (ref. 1). Figure 1 gives a typical plot of the smooth increase of b with time, and shows that the 2,2-dinitropropanol dissociates to $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ at a rate which decreases with time. The equilibrium value of b is approached asymptotically, and indicates only partial dissociation of the 2,2-dinitropropanol.

EQUILIBRATION MECHANISM

Two reasonable equilibration mechanisms, (1) or its equivalents and (2),



are kinetically distinguishable. However, only (1) is consistent with the observed concentration dependence of the initial rate, $(\text{dB}/\text{dt})_0$. Now, $(\text{dB}/\text{dt})_0$, measured on a solution which is approaching equilibrium from complete dissociation is a very good approximation to the association rate. Experimentally, we find that $(\text{dB}/\text{dt})_0 \propto B^2$, as predicted by mechanism (1), thus eliminating mechanism (2) which predicts that $(\text{dB}/\text{dt})_0 \propto B$. On this basis we shall assume that (1) is the equilibration mechanism, and see whether the observed rate data fit the integrated rate equation required by (1), equation (6) (see Appendix).

TABLE I
SUMMARY OF SECOND ORDER RATE CONSTANTS FOR REACTION (1)
(IONIC STRENGTH = 0.1)

Temp., °C	pH	Run No.	k_2^a	$10^{-5}k_1^a$		
25.13	6.68	1	31.92	11.84		
		2	31.72			
		3	31.94			
		4	31.87			
	6.37	1	32.12			
		2	31.69			
	6.08	1	32.14			
		2	31.89			
	<hr/>					
	overall average 31.91					
	9.64	6.73	1		8.63 ₇	3.30 ₇
			2		8.42 ₈	
3			8.37 ₅			
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overall average 8.48 ₀						

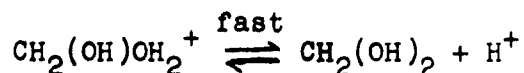
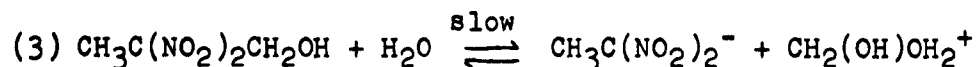
a In units of liter-mol⁻¹-min.⁻¹

RESULTS

We find that the rate data for three pH's at 25.13° and one pH at 9.64° do indeed fit equation (6) quite well. For each kinetic run, Table I gives the bimolecular rate constant for the reaction of $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ and $\text{CH}_2(\text{OH})_2$, k_2 , calculated from equation (6) using the Guggenheim treatment of the rate data and the method of least squares for finding the best fit. Since the rather narrow range of k_2 values for each pH at 25.13° is about the same, the average k_2 for 25.13° was calculated using all eight k_2 's. Finally, the bimolecular rate constant for the reaction of $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$ and OH^- , k_1 , was calculated as k_2K , using, for each temperature, the overall average k_2 value and the equilibrium constant for reaction (1), K , taken from reference 1.

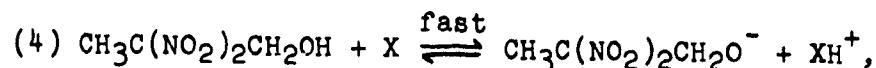
DISCUSSION

The pH-independence of k_2 makes the dissociation of the 2,2-dinitropropanol subject to specific catalysis by hydroxide ion, with no detectable catalysis by $\text{HPO}_4^{=}$ or H_2PO_4^- (see Appendix B). On this basis we can assuredly rule out equilibration mechanism (3): The integrated rate equation required by (3) is of the same form as (6), and will, of course, fit our

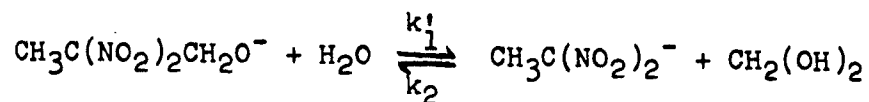


rate data at any one pH; however, the rate of association of $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ and $\text{CH}_2(\text{OH})_2$ will be proportional to, rather than independent of, the activity of hydrogen ion.

The lack of catalysis by $\text{HPO}_4^{=}$ is rather surprising, because $\text{HPO}_4^{=}$ has nearly the same nucleophilicity toward carbon as OH^- (reference 3), and the concentration of $\text{HPO}_4^{=}$ is about 10^6 times the concentration of OH^- in the buffers used for our rate measurements (see Appendix B). This apparent anomaly can be rationalized if equilibration mechanism (1) is replaced by its kinetic equivalent, mechanism (4). In (4), specific hydroxide ion catalysis



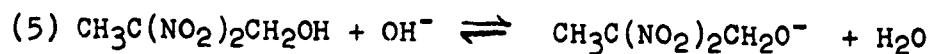
X = general base



of the dissociation of $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$ will be observed when the general base is HPO_4^{2-} , H_2PO_4^- , OH^- etc. According to mechanism (4), the rate of association of $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ and $\text{CH}_2(\text{OH})_2$ is

$k_2[\text{CH}_3\text{C}(\text{NO}_2)_2^-][\text{CH}_2(\text{OH})_2]$, and the dissociation rate is

$k_1'K'a[\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}]$, where a is the activity of hydroxide ion and K' is the equilibrium constant for (5). In other words, the



interpretation of k_2 is the same for mechanism (1) and (4), but the dissociation rate constant for (1), k_1 , is actually $k_1'K'$, in terms of mechanism (4). Clearly, experiments should be designed to evaluate the unknown K' so that k_1' can be evaluated. One can rationalize the precedence of mechanism (4) over (1) as follows: The transition state for the dissociation of $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$ or $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}^-$ requires that negative charge be transferred to the 2-carbon and its nitro groups; it may well be that negative charge can be more readily transferred from the negative oxygen of $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{O}^-$ than from OH^- .

Values of the activation energy, E_a , ΔH^\ddagger and ΔS^\ddagger for the association of $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ and $\text{CH}_2(\text{OH})_2$ are listed in Table II. These quantities were calculated from the overall average k_2 values at 25.13 and 9.64° and the standard equations which result from the transition state theory for unimolecular gas reactions (reference 5). The analogous calculations for the dissociation reaction were not made because the value of K' is unknown. The loss of entropy when the transition state is formed from $\text{CH}_3\text{C}(\text{NO}_2)_2^- + \text{CH}_2(\text{OH})_2$ can be rationalized as follows: The water solvating the transition state is more specifically oriented than the water solvating the carbanion $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ because the negative charge of the carbanion is more dispersed than that of the transition state. Finally, it is clear that the high ratio of $k_1'K'$ to k_2 is almost solely caused by the large positive ΔS for reaction (1) (see Table II); the large negative ΔS^\ddagger for the association reaction accounts for most of the ΔS for (1) if ΔS for (5) is small.

TABLE II
THERMODYNAMIC AND PSEUDOTHERMODYNAMIC CHANGES INVOLVED
IN THE EQUILIBRATION OF 2,2-DINITROPROPANOL IN WATER

Quantity Calculated	For the Formation of the Transition State for the Reaction of $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ and $\text{CH}_2(\text{OH})_2$	For Reaction (1) (Overall Change) ^a
E_a , kcal	14.3	-
ΔH , kcal	13.7	-0.5
ΔS , e.u. ^b	-13.7	19.1

a. Taken from reference 1.

b. Calculated by using values of k_2 in units of liter-mol⁻¹-sec.⁻¹

EXPERIMENTAL

Apparatus and Measurements.

HPO_4^- - H_2PO_4^- buffers and pH measurements were made by the procedures described in reference (1), using only one buffer conc. for each pH. This reference also describes the optical density measurements, the thermostatted cell compartment, and the source of the 2,2-dinitropropanol. The path length of the sample cell, 0.0299 cm., is that stated by the manufacturer, The American Instrument Company, Silver Spring, Maryland.

Initial Association Rates. Temperature = $25.02 \pm 0.02^\circ\text{C}$.
pH = 6.8

2.000 ml. of a stock solution of 2,2-dinitropropanol in water was diluted to 100 ml. with 0.1 N aqueous NaOH. The optical density of this solution at λ_{max} for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$, 382 mμ, was 0.301.

2.000 ml. of the same stock solution of 2,2-dinitropropanol, 23.65 ml. of 0.1 N aqueous NaOH, 50.00 ml. of 0.1 M aqueous KH_2PO_4 was diluted to 100 ml. with distilled water. Another

solution was made in the same way using the same buffer components and 4.000 ml. of the dinitropropanol stock solution. The optical densities of these solutions was measured at 382 mμ versus time as soon as temperature equilibration was attained (about one minute). Table III gives the optical density-time data. The optical density measurements were converted to values of $[\text{CH}_3\text{C}(\text{NO}_2)_2^-]$, using the molar extinction coefficient for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ at λ_{max} for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$, 382 mμ, as $=1.777 \times 10^4$ (reference 1). The initial slopes of the plots of $[\text{CH}_3\text{C}(\text{NO}_2)_2^-]$ versus time were then determined graphically.

TABLE III

DATA USED TO CALCULATE INITIAL ASSOCIATION RATES

Time, Min.	Optical Density at 328 mμ, x ml. of 2,2-Dinitropropanol Stock Solution Used	
	x = 2.000	x = 4.000
0.00	0.287	0.547
0.37	0.285	-
0.66	-	0.539
1.04	0.281	-
1.32	-	0.528
1.90	0.279	-
2.28	-	0.513
2.60	0.277	-
3.01	-	0.503
3.35	0.274	-
3.82	-	0.496
4.05	0.273	-
4.50	0.271	-
4.60	-	0.487
5.19	0.269	-

Equilibration Rates.

A volume v_{NaOH} of an aqueous stock solution of 2,2-dinitropropanol was diluted to a volume V_{NaOH} with 0.1 N aqueous NaOH; the optical density at 382 mμ, b_{NaOH} , was then measured at constant temperature. A volume v of the same stock solution of

2,2-dinitropropanol, the appropriate buffer components, and sufficient aqueous 1 M NaCl to make the final ionic strength 0.1 were diluted to a volume V; the optical density of this solution at 382 m μ was then measured at constant temperature versus time after temperature equilibration (about one min.). Table IV summarizes the volumetric data, and Tables V and VI the rate data for 25.13 and 9.64° respectively.

TABLE IV
VOLUMETRIC DATA FOR SOLUTIONS USED TO MEASURE
EQUILIBRATION RATES

Temp., °C.	pH	Run No.	v _{NaOH} , ml.	V _{NaOH} , ml.	b _{NaOH}	v, ml.	V, ml.
25.13	6.68	1	2.500	249.91	0.417	2.400	100.01
		2*	2.500	249.91	0.417	2.357	100.01
		3*	2.500	249.91	0.417	2.340	100.01
		4*	2.500	249.91	0.417	2.375	100.01
	6.37	1	2.504	249.91	0.458	3.093	100.01
		2*	2.504	249.91	0.458	3.110	100.01
	6.08	1	2.512	100.04	0.414	4.977	100.01
		2*	2.512	100.04	0.414	4.985	100.01
9.64	6.73	1	2.003	100.04	0.490	4.137	100.04
		2*	2.003	100.04	0.490	4.576	100.04
		3	2.616	250.30	0.410	3.079	100.04

*Same stock solution of 2,2-dinitropropanol as used for run No. 1; values of v_{NaOH}, V_{NaOH}, and b_{NaOH} are those determined for run No. 1 and are not redeterminations.

TABLE V

OPTICAL DENSITY-TIME DATA FOR 25.13°C.

Time, min.	pH 6.68				pH 6.37		pH 6.08	
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 1	Run 2
0.00*	0.414	0.417	0.423	0.422	0.447	0.421	0.411	0.412
0.75	0.432	0.432	0.438	0.437				
1.00					0.464	0.432	0.423	0.427
1.50	0.448	0.447	0.451	0.452				
2.00					0.478	0.452	0.432	0.433
2.25	0.459	0.459	0.462	0.463				
3.00	0.472	0.469	0.472	0.474	0.489	0.462	0.442	0.443
4.00	0.487	0.484	0.487	0.489			0.451	0.454
5.00	0.500	0.497	0.498	0.502		0.488		0.462
5.50					0.517		0.462	
6.00	0.513	0.507	0.509	0.512		0.499		
6.50								0.472
7.00	0.522	0.517	0.518	0.522	0.522	0.508	0.473	
8.00	0.532	0.523			0.530			0.482
8.50			0.532	0.538		0.521	0.482	
9.50	0.544	0.538			0.542			0.489
10.00			0.540	0.547		0.531	0.491	
11.00	0.552	0.545			0.550			0.501
12.00						0.547	0.500	
13.00			0.556	0.562				0.503
13.50					0.562			
14.00	0.569	0.560						
15.00						0.558	0.510	
15.50					0.568			
16.50								0.519
18.00						0.571		
19.00					0.578		0.527	
20.00								0.532
21.00						0.577		
24.50							0.537	
25.00					0.589			0.539
28.00							0.538	
equil.	0.597	0.587	0.584	0.593	0.597	0.598	0.553	0.557

*Zero is arbitrary. Timer was started as soon as temperature equilibration was attained (about one minute).

TABLE VI
OPTICAL DENSITY-TIME DATA FOR 9.64°C. AND pH 6.73

Time, min.	Run No. 1	Run No. 2	Run No. 3
0.00*	0.267	0.292	0.289
3.00	0.279		
4.00			0.303
6.00	0.289		
8.00		0.301	
9.00		0.314	0.318
10.00	0.297		
14.00		0.326	0.329
15.00	0.309		
20.00		0.338	0.345
21.00	0.319		
28.00	0.329		0.362
29.00		0.352	
35.00		0.364	
38.00	0.345		
40.00			0.384
45.00		0.378	
48.00	0.362		
50.00			0.402
60.00	0.374		
61.00		0.395	
63.00			0.418
75.00	0.386	0.409	
76.00			0.429
90.00	0.394		
91.00		0.419	
100.00			0.446
120.00	0.408	0.430	
equil.	0.427	0.448	0.469

*Zero is arbitrary. Timer was started as soon as temperature equilibration was attained (about one minute).

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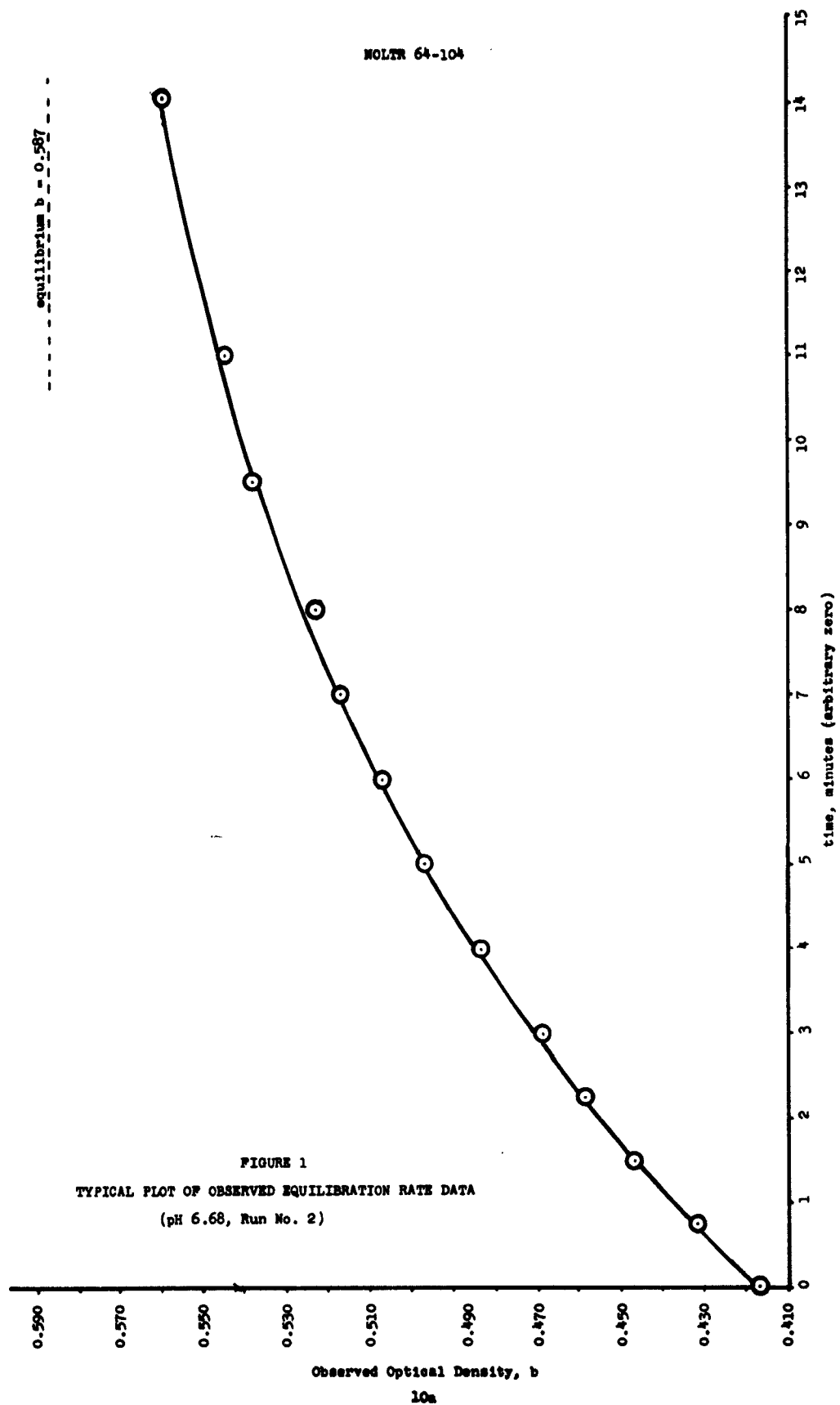
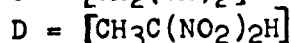
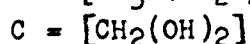
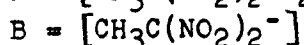
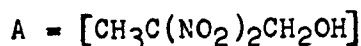


FIGURE 1
TYPICAL PLOT OF OBSERVED EQUILIBRATION RATE DATA
(pH 6.68, Run No. 2)

APPENDIX A

Derivation of Integrated Rate Equations Required by Equilibration Mechanism (1).
Summary of Calculations.

1. The following symbols will be used:



k_1 = second order rate constant for the dissociation reaction in equation (1)

k_2 = second order rate constant for the association reaction in equation (1)

K = equilibrium constant for reaction (1) = k_1/k_2

K_1 = ionization constant for $\text{CH}_3\text{C}(\text{NO}_2)_2\text{H}$

$R = (B+D)/B = 1 + a'/K_1$

ϵ = molar extinction coefficient for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ at λ_{max} for $\text{CH}_3\text{C}(\text{NO}_2)_2^-$ (382 m μ)

l = path length of the cell used to measure rates

b = optical density at 382 m μ of the equilibrating solution
 $\epsilon l B$

t = time (minutes used in our experiments)

Subscripts o and e denote initial and equilibrium values
 a and a' are the activities of hydroxide and hydrogen ion, respectively

2. Concentration relations.

Since we start with pure 2,2-dinitropropanol, $B_o = C_o = 0$. Then, from the stoichiometry of equation (1), $A_o = A_e + B_e + D_e = A_e + RB_e$, and $A = A_o - RB = A_e + RB_e - RB = B_e C_e / K_a - RB = R(B_e^2 / K_a + B_e - B)$.

3. Rate Equation in differential form.

From eq.(1), $dB/dt = k_1 aA - k_2 BC$, or, from 2. above, $dB/dt = k_2 R [B_e (B_e + K_a) - K_a B - B^2]$. In this rate equation, we have assumed that concentration and activity are the same for

$\text{CH}_3\text{C}(\text{NO}_2)_2^-$, $\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{OH}$, and $\text{CH}_2(\text{OH})_2$. This assumption probably does not introduce a significant error because the solutions are dilute; reference 1 estimates the magnitude of these errors.

4. Integrated rate equation.

On integration of the differential rate equation, 3. above, between the limits of $B = 0$ ($t = 0$) and $B(t)$, we obtain

$$1/(2B_e + Ka) \ln \left[\frac{(B_e - B)(B_e + Ka)}{B_e(B_e + B + Ka)} \right] = -k_2 R t. \quad \text{In terms of } b, \text{ the}$$

latter becomes,

$$\epsilon l / (2b_e + Ka \epsilon l) \ln \left[\frac{(b_e - b)(b_e + Ka \epsilon l)}{b_e(b_e + b + Ka \epsilon l)} \right] = -k_2 R t.$$

5. We can evaluate k_2 from the above equation in b by applying the Guggenheim treatment for first order reactions (reference 6). If the value of b for time $(t + \Delta)$ is b' , we find from 4. above

$$\frac{(b_e - b)(b_e + Ka \epsilon l)}{b_e(b_e + b + Ka \epsilon l)} = \exp \left[-k_2 R t (2b_e + Ka \epsilon l) / \epsilon l \right], \text{ and,}$$

$$\frac{(b_e - b')(b_e + Ka \epsilon l)}{b_e(b_e + b' + Ka \epsilon l)} = \exp \left[-k_2 R (t + \Delta) (2b_e + Ka \epsilon l) / \epsilon l \right].$$

Subtracting these two equations, we get equation (6).

$$(6) \ln \left[\frac{b_e - b'}{b_e + b' + Ka \epsilon l} - \frac{b_e - b}{b_e + b + Ka \epsilon l} \right] =$$

$$-k_2 t (1 + a'/K_1) (2b_e + Ka \epsilon l) + c,$$

where

$$e^c = b_e / (b_e + Ka \epsilon l) \left[-\exp(-k_2 R \Delta (2b_e + Ka \epsilon l) / \epsilon l) + 1 \right].$$

6. Least square treatment of kinetic data.

Equation (6) is of the standard slope-intercept form for the equation of a straight line: $y = mx + c$, and hence is readily adaptable to least-square calculation of k_2 . For each run, a smooth plot of b versus t was drawn to obtain the values of b and t required to use equation (6). Least-square values of $Rk_2/\epsilon l$ and c for each kinetic run were calculated using the IBM 7090 computer, and are summarized in Table VII. The value of the intercept constant c is the value which gives the best least-square fit; it should be noted that this intercept constant actually contains k_2 (see equation (6)). Values of k_2 calculated from c are not as precise as those calculated from the slopes, but did agree well with the latter. The standard deviation listed in Table VII was calculated as follows for each Δ : For each value of t used in the least-square calculation, the difference, d , between the least-square c and the actual c , calculated from the observed data and the least-square value of $k_2 R/\epsilon l$, was found. The standard deviation in c listed in Table VII was then calculated as $\Sigma d^2/(n-1)$, where N is the number of sets of b - t data used in the least-square calculation of $k_2 R/\epsilon l$. Finally, the average values of K , ϵ and K_1 taken from reference 1 were used to calculate the rate constants listed in Table I.

TABLE VII. SUMMARY OF CALCULATIONS

A	Run No. 1			Run No. 2			Run No. 3			Run No. 4		
	$10^3 R_{\text{H}_2}/eL$	-c	Std.Dev.	$10^3 R_{\text{H}_2}/eL$	-c	Std.Dev.	$10^3 R_{\text{H}_2}/eL$	-c	Std.Dev.	$10^3 R_{\text{H}_2}/eL$	-c	Std.Dev.
pH 6.68 (25.13°C)												
6	6.057	2.972	0.014	6.148	3.048	0.010	6.166	3.034	0.021	6.105	3.032	0.019
7	6.072	2.872	0.013	6.166	2.948	0.011	6.180	2.935	0.015	6.111	2.933	0.015
8	6.098	2.792	0.010	6.119	2.872	0.012	6.213	2.855	0.013	6.107	2.855	0.010
9	6.177	2.724	0.010	6.125	2.808	0.009	6.141	2.800	0.014	6.167	2.788	0.008
10	6.268	2.668	0.010	6.173	2.753	0.006	6.240	2.744	0.013	6.220	2.734	0.006
11	6.380	2.621	0.008	6.093	2.711	0.006	6.134	2.706	0.008	6.292	2.690	0.006
	av. 6.175			av. 6.137			av. 6.179			av. 6.167		
pH 6.37 (25.13°C)												
7	6.317	2.987	0.013	6.363	2.743	0.018						
8	6.333	2.898	0.012	6.340	2.627	0.015						
9	6.374	2.822	0.010	6.327	2.584	0.012						
10	6.373	2.763	0.008	6.291	2.525	0.010						
11	6.443	2.705	0.005	6.277	2.474	0.007						
12	6.535	2.655	0.004	6.268	2.431	0.005						
	av. 6.396			av. 6.311								
pH 6.08 (25.13°C)												
10	6.761	2.629	0.040	6.705	2.640	0.035						
11	6.728	2.574	0.033	6.656	2.585	0.027						
12	6.714	2.525	0.028	6.626	2.539	0.021						
13	6.670	2.485	0.020	6.636	2.494	0.016						
14	6.653	2.449	0.015	6.647	2.456	0.013						
15	6.678	2.415	0.011	6.652	2.424	0.010						
16	6.742	2.383	0.009	6.666	2.395	0.007						
17	6.797	2.356	0.004	6.713	2.368	0.005						
18	6.812	2.335	0.003	6.767	2.344	0.004						
	av. 6.728			av. 6.674								
pH 6.73 (9.64°C)												
28	1.692	2.763	0.030	1.731	2.721	0.075	1.694	2.541	0.062			
32	1.702	2.662	0.023	1.703	2.634	0.062	1.675	2.450	0.052			
36	1.699	2.585	0.015	1.673	2.566	0.053	1.666	2.370	0.046			
40	1.702	2.513	0.011	1.684	2.502	0.042	1.658	2.302	0.041			
44	1.706	2.450	0.009	1.640	2.445	0.032	1.646	2.245	0.034			
48	1.706	2.397	0.008	1.638	2.393	0.028	1.640	2.193	0.029			
52	1.708	2.349	0.008	1.635	2.346	0.022	1.636	2.148	0.025			
56	1.705	2.309	0.009	1.634	2.305	0.016	1.626	2.111	0.018			
60	1.704	2.272	0.008	1.642	2.265	0.013	1.618	2.077	0.013			
64	1.704	2.241	0.009	1.654	2.229	0.010						
68	1.700	2.213	0.009	1.665	2.197	0.008						
	av. 1.702			av. 1.661			av. 1.651					

APPENDIX B.

Discussion of Catalysis of the Carbinol Dissociation Reaction, (1), by $\text{HPO}_4^{=}$ and $\text{H}_2\text{PO}_4^{-}$.

If the dissociation reaction were catalyzed by $\text{HPO}_4^{=}$, $\text{H}_2\text{PO}_4^{-}$, and OH^{-} , then the rate of this reaction would be of the form $A[k_a + k'[\text{HPO}_4^{=}] + k''[\text{H}_2\text{PO}_4^{-}]]$. This expression reduces to the observed form k_2aA under either of the following conditions: (i) $[\text{HPO}_4^{=}]$ and $[\text{H}_2\text{PO}_4^{-}]$ are proportional to a , or (ii) rates due to $\text{HPO}_4^{=}$ and $\text{H}_2\text{PO}_4^{-}$ are negligible compared to the hydroxide ion rate. We find from the composition of the buffers used for our rate measurements (given in reference 1) that the proportionalities required by (i) do not exist: for pH 6.08, $a = 1.21 \times 10^{-8}$, $[\text{HPO}_4^{=}] = 0.0070$, $[\text{H}_2\text{PO}_4^{-}] = 0.043$; for pH 6.68, these quantities are 4.82×10^{-8} , 0.019, and 0.031, respectively.

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